

Vapour phase purification of liquids

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Abstract of GB1030214

Esters or linear polyesters of molecular weight at least 400 and below 5000, are purified by passing a stream downwardly through a fractionating column with a gas-liquid contacting means and an inert gas stream upwardly at a temperature at least 100 DEG C. and a linear velocity of from 3 to 100 feet per second, and collecting the ester or polyester at the base. The ester is preferably preheated to 100 DEG to 250 DEG C. and is neutralized before or after the stripping stage. Superheated steam, nitrogen, methane and propane may be the inert gases and esters specified are didecyl and dioctyl phthalate, bis - (2,2,4 - trimethylpentyl) azelate, 2,2,4-trimethylpentane - 1,3 - dipelargonate, glycerine triesters and the pelargonate of trimethylol propane and the polyesters are reaction products of a diol and dicarboxylic acid terminated with a monohydric alcohol or monocarboxylic acid and lists of glycols, dicarboxylic acids and terminating compounds are given. The invention is also particularly applicable to esters prepared from dicarboxylic acid and glycol monoesters with a secondary hydroxyl group in the 3-position, in the presence of tin catalysts and compounds of lower boiling point are stripped from the product. ALSO: Linear polyesters of molecular weight at least 400 and below 5000 are purified by passing a stream downwardly through a fractionating column with a gas-liquid contacting means, and an insert gas stream upwardly at a temperature at least a 100 DEG C. and a linear velocity of from 3 to 100 feet per second, and collecting the polyester at the base. The ester is preferably preheated at 100 to 250 DEG C. and is neutralized before or after the stripping stage. Superheated steam, nitrogen, methane and propane may be the inert gases and polyesters specified are the reaction products of a diol and dicarboxylic acid terminated with a monohydric alcohol or a monocarboxylic acid and lists of glycols, dicarboxylic acids and terminating compounds are given. The invention is also particularly applicable to esters prepared from dicarboxylic acid and glycol monoesters with a secondary hydroxyl group in the 3-position in the presence of tin catalysts and compounds of lower boiling point are stripped from the product.

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COMPLETE SPECIFICATION

Vapour Phase Purification of Liquids

We, EASTMAN KODAK COMPANY, a Company organized under the laws of the State of New Jersey, United States of America of 343 State Street, Rochester, New York 14650, United States of America (Assignees of DAVID CARLOCK HULL and HUGH JOHN HAGEMeyer Jr) do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the purification of esters.

Vinyl polymers and co-polymers and cellulose esters used for plastic moulded articles, sheeting, films, etc are normally plasticised with diesters derived from monohydric alcohols and dicarboxylic acids. The plastic composition will contain, for example, 5 to 50 parts of plasticiser ester per 100 parts of resin. To avoid loss of the plasticiser by vapourisation from the plastic composition the trend in recent years has been to use plasticisers of greater permanency such as monomeric diester plasticisers obtained from high molecular weight monohydric alcohols or polymeric plasticisers obtained by reaction of a diol with a dicarboxylic acid and terminated with a monohydric alcohol or a carboxylic acid. These esters and polyesters have molecular weights greater than 400 and have exceedingly low vapour pressure at atmospheric pressure. They cannot be refined by normal techniques such as high vacuum distillation or molecular distillation without considerable change in the equilibrium composition or decomposition of the product. The decomposition results in low yields, high odour and poor colour. With the polyesters considerable trans-esterification takes place. This leads to products of such high molecular weight that they are not suitable as

plasticizers.

We have now discovered a novel purification method which is applicable to high molecular weight diesters of monohydric alcohols and dicarboxylic acids and to linear polyesters of a molecular weight suitable for polymeric plasticisers, i.e. below 5000. Our procedure is particularly applicable to compounds that are heat sensitive, such as linear polyesters produced from dicarboxylic acids and 1,3-diols having a secondary hydroxyl group, such diols being highly susceptible to dehydration.

According to the present invention there is provided a method of purifying an ester or linear polyester having a molecular weight of at least 4400 and below 5000 which comprises passing a stream of the impure ester or polyester downwardly through a fractionating column having a gas-liquid contacting means and a stream of inert gas at a temperature of at least 100° C upwardly through the column at a linear velocity of from 3 to 100 feet per second, the purified ester or polyester being collected from the base of the column.

In general, the process of our invention by which we recover high molecular weight esters or linear polyesters that are essentially odour free and of low colour comprises continuously introducing a stream of the crude or unpurified liquid ester of molecular weight in the range of 400 to 5000 to the upper end of a stripping column provided with vapour-liquid contacting means, continuously introducing at the lower end of such column in counter-current flow to the stream of said ester in a stream of an inert gas at a temperature of 100 to 250° C and at a linear velocity greater than 3 feet per second. The inert gas and stripped impurities are withdrawn overhead from the column and the purified liquid ester or polyester is withdrawn from the bottom. In preferred embodiments of the process by

which the highest quality products are obtained, the unpurified liquid ester or polyester is preheated to a temperature of 100 to 250° C before introduction into the upper end of the stripping column and is neutralised by caustic treatment before or after the stripping stage.

The preferred inert carrier gas for our process is superheated steam. However, other inert gases such as nitrogen, methane, ethane and propane, can be used. Although we operate at elevated temperatures in the range of 100 to 250° C, the effective force by which separation of the impurities from the ester is accomplished is the kinetic energy of the carrier gas, $K = mV^2/2$, where m is the weight of the gas and V is the linear velocity.

The process of our invention is readily distinguishable from steam distillation and azeotropic distillation wherein organic liquids are distilled with large volumes of steam. Our process employs a combination of the use of a temperature substantially above that normally employed for steam distillation, the use of an unusually high linear velocity of the inert gas and the countercurrent contact of the downflowing liquid and the upflowing inert gas in a column provided with vapour-liquid contacting means such as packing, or bubble cap trays.

In steam and azeotropic distillations the ratio of organic liquid to water distilled overhead is a function of the partial pressure of the organic liquid. The steam requirements for the high molecular weight esters and polyesters such as are purified in accordance with our invention would ordinarily be from 50 to 100 pounds per pound of ester or polyester if conventional methods were used. However, we have found that when the kinetic energy of the steam is increased by virtue of its high linear velocity, the ratio of organic liquid to steam is no longer a primary function of partial pressure and efficient separation is accomplished at steam to organic ratios of 1:1 to 10:1. A further advantage is that our process employs low hold-up time in the fractionating column. This eliminates or reduces such side reactions as pyrolysis, dehydration, hydrolysis and transesterification.

The esters which can be purified by this invention include the so-called monomeric plasticiser esters which are the reaction products of a dicarboxylic acid or a dicarboxylic acid anhydride with a monohydric alcohol or the reaction products of polyhydric alcohols or diols with monocarboxylic acids. Representatives of this class include didecyl phthalate, dioctyl phthalate, bis(2,2,4-trimethylpentyl)azelaate, 2,2,4-trimethylpentane-1,3-dipelargonate, glycerine triesters and the pelargonate of trimethylol propane.

The polyesters which can be purified by this invention comprise the polyester plasticisers which are reaction products of a diol

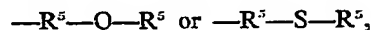
and a dicarboxylic acid, and which are terminated with a monohydric alcohol or with a monocarboxylic acid. The average molecular weight of such plasticiser polyesters will range from about 500 to 5000 and preferably about 500 to 1500.

Suitable glycols for preparing such polyesters include glycols of the type,



wherein R^1 is a straight or branched alkylene radical of from 2 to 10 C atoms. Examples include ethylene glycol, propylene glycol, neopentyl glycol, 2,4-dimethyl-2-ethylhexane-1,3-diol, 2,2,4-trimethylpentane-1,3-diol, butane-1,4-diol, pentane-1,5-diol and hexane-1,6-diol.

Suitable dicarboxylic acids include acids of the type, $\text{HOOC}-\text{R}^2-\text{COOH}$, wherein R^2 is a divalent organic radical such as a straight or branched alkylene or alkenylene radical of 1 to 8 C atoms; a divalent alicyclic radical; a phenylene or substituted phenylene radical, preferably of 6 to 9 C atoms, in which the carboxyl groups are in the *o*-, *m*- or *p*-positions; oxygen or a radical such as



wherein R^5 is a lower alkylene radical, e.g. of from 1 to 4 C atoms. R can also be simply a covalent bond, in which event the acid is oxalic acid.

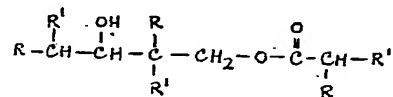
Examples of such dicarboxylic acids include oxalic, malonic, succinic, glutaric, adipic, trimethyl adipic, 2,2-dimethylglutaric, azelaic, sebacic, fumaric, maleic, itaconic, 1,4-cyclohexanedicarboxylic, phthalic, terephthalic, isophthalic, diglycolic and thiopropionic. Corresponding acid anhydrides can also be used in the esterification reaction and we use the term "acid" to include such anhydrides.

Suitable terminating acids or alcohols include aliphatic monocarboxylic acids or aliphatic monohydroxy alcohols of 2 to 10 C atoms, e.g. isobutyric acid, 2-ethylhexanoic acid, isobutanol and 2-ethylhexanol.

Reaction products having at least a minor polyester content are also obtainable by the reaction of glycol monoesters with dicarboxylic acids. A valuable ester of this type for which the process of our invention is particularly applicable is formed by the reaction of a dicarboxylic acid of the type,



above, with a glycol monoester of the formula



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wherein R and R' are the same or different lower alkyl radicals such as methyl, ethyl, propyl, isopropyl, butyl and isobutyl. Such glycol monoesters can be prepared by the

5 Tischenko trimolecular condensation of an aldehyde having a single α -hydrogen atom, e.g. isobutyraldehyde, in the presence of a metal alkoxide catalyst: Tischenko et al, *Chem. Zentr.* 1906, II, 1552—1556; Villani and Nord, *J. Am. Chem. Soc.* 69, 2605 (1947).

The glycol monoesters (I) and the glycol moieties thereof have a secondary hydroxyl group in the 3-position and present a special problem in esterification reaction. However, they can be successfully esterified with dicarboxylic acids in the presence of organic tin catalysts as disclosed in our application 43346/62 1030213 to yield valuable plasticiser esters or polyesters of the type "monobasic acid-diol (diacid-diol), monobasic acid," where n is an integer from 1 to 10 such products having an average molecular weight of about 500 to 1500.

15 In the process of that invention wherein the esterification is effected using a dicarboxylic acid, such as when producing substances of formula II, compounds of lower boiling point are produced as well as of higher boiling point. The lower boiling point compounds may be stripped from the other compounds by the method provided by this invention according to which a stream of the mixture of compounds flows against a stream of hot inert gas at high linear velocity. Thus, in separating low boiling point compounds from substances of formula II sparge stream at an initial temperature of 100 to 125° C or preferably higher, e.g. about 190° C, and flowing in a stream at from 3 to 5 feet per second may be used or 0.9 metres per second. Nitrogen or methane may be used as the inert gas.

25 The purification procedure of the present invention is beneficial in general for polyesters derived from (I) and glycols corresponding to the glycol moiety thereof because such reaction products contain as impurities certain undesirable by-products formed as a result of the dehydration of the secondary hydroxyl group.

Purified high molecular weight monomeric and polymeric ester plasticisers that are essentially odourless and of little colour are prepared by a combination of procedures including our novel gas stripping procedure. In one embodiment the combination comprises (a) esterification, (b) neutralisation, (c) gas stripping and (d) drying and filtration. The steps can also follow the order: (a) esterification, (b) gas stripping, (c) neutralisation and (d) drying and filtration. The order followed will depend on the choice of stripping gas and on the composition of the reaction mixture. The drying step can be eliminated if the stripping

step follows the neutralisation step and if a dry stripping gas is used. 65

ESTERIFICATION

The esterification stage can employ conventional procedure for producing high molecular weight diesters and liquid polyesters. Suitable catalysts include mineral acids, acid halides, aryl sulphonic acids, metal halides and metal alkoxides. For materials which are heat sensitive or susceptible to dehydration such as the 1,3-diols having a secondary hydroxyl group, we employ tin catalysts such as stannous or stannic hydroxide, the dialkyl tin dialkoxides, the dialkyl and tetralkyl tins and the dialkyl tin oxides. The esterification is normally carried out in the presence of an excess of the more volatile of the reactants plus an azeotroping agent to facilitate removal of water. The choice of azeotroping agent and the amount thereof depends upon whether or not it is used to control the reaction temperature. Suitable azeotroping agents include diethyl ether, diisopropyl ether, ethylene dichloride, benzene, toluene, xylene, hexane, and heptane. The esterification temperature will range from about 50 to 250° C. The reaction time will range from about 4 to 48 hours depending on the product being made. 70 75 80 85 90

When the esterification is completed the crude reaction product is normally subjected to either a caustic wash or a neutralisation procedure. Alternatively, this step can follow the inert gas stripping operation. However, it is preferred that the stripping step follow the neutralisation step, because as indicated above, this sequence makes it possible to eliminate subsequent drying if a dry stripping gas is used. 95 100

NEUTRALISATION

In the caustic washing operation the crude ester is fed to an alkali wash column and washed countercurrently at a temperature of 20 to 80° C with a stream of a dilute alkali solution containing 5 to 15% alkali in a volume ratio of aqueous caustic to organic liquid of 1:2 to 1:1. Following the alkali wash the organic layer is decanted and fed to a water wash column to remove residual alkali. The organic feed is then decanted and is ready for feed to the gas stripping stage. 105 110

Preferably, the crude ester, instead of being washed with dilute aqueous caustic, is neutralised by treatment with more concentrated caustic in an amount only moderately in excess of the stoichiometric amount. This procedure offers important advantages over dilute caustic washing. The high molecular weight esters, particularly the polyesters, require a long time to separate after caustic washing. Some show no tendency to separate even after 48 hours and solvents must be used. Often a middle phase persists even when large volumes of solvent are used. This middle layer 115 120 125

is an organic water emulsion which must be broken by adding more solvent or caustic to the mixture, or it must be set aside for separate treatment. If the middle layer is combined with the organic feed to the gas stripper, large quantities of water will be present in the feed. As much as 35 weight % water has been noted. This causes flooding of the column, loss of temperature control, and poor product quality. Even when no emulsion is present the organic feed to the gas stripper is found to contain as much as 15% water. The water carries large quantities of caustic and salts into the stripping column and these deposit on the column packing. If the emulsion layer is discarded the yield of product may be cut as much as 30%.

The emulsion problem can be overcome by using more concentrated caustic solutions, e.g. up to 20%, for the caustic wash, or by dilution of the reaction mixture with a lower density solvent (up to 80% solvent has been required), or by the use of higher temperatures for washing (70 to 90° C). All these procedures have disadvantages.

Preferably, therefore, the alkali and water washing steps are replaced by the simple neutralisation step in which the crude ester is treated with sufficient aqueous caustic to neutralise any unreacted acid. Only a small quantity of aqueous caustic is used and there is no separation of the organic and aqueous phases. The amount of caustic can vary from a 50% molecular excess to an 100% molecular excess or up to twice the stoichiometric amount. A typical neutralisation by this procedure would require 1 gallon of 20% caustic for 6000 pounds of crude ester. To determine the amount of caustic required the acid number (mg of KOH required to neutralise 1 g. of sample) and the total weight of the material to be neutralised are determined. The total weight of caustic required to neutralise the free acid in the product is then calculated. This amount plus a 50 to 100% excess is added to the crude ester as an aqueous solution of 10 to 25% concentration. The mixture is agitated for 1 to 3 hours at 25 to 30° C and is then ready for drying and filtering or for the gas stripping step.

GAS STRIPPING

In a typical operation of the stripping step, the crude ester, with or without prior neutralisation, is preheated to 100 to 250° C and is fed to a point in the upper half of the stripping column which is provided with vapour-liquid contacting means, such as inert packing materials, bubble cap trays, perforated trays or the like. The inert gas such as steam, nitrogen, methane or ethane, preferably preheated to about the same temperature as the ester feed, is fed to a point near the bottom of the stripping column and is counter-currently contacted with the downflowing

organic liquid at a high linear velocity. The height of the column above the organic feed point depends upon the degree of fractionation desired. With a proper selection of temperature, and of the mass and linear velocity of the inert gas stream, fractionation of esters or polyesters with molecular weights from 400 to 5000 can be readily achieved. The vapour velocity, i.e. the effective relative linear velocity of the stripping gas as it contacts the organic liquid, is a critical element of our process. The vapour velocities employed in our stripping procedure range from 3 to 100 feet per second and are thus substantially higher than those conventionally employed in distillation columns. Our preferred linear velocities of the stripping gas are in the range of 3 to 10 feet per second.

In our process we use the kinetic energy of the carrier gas and through the use of an appropriate volume of inert gas, depending on its mass, and a suitably high linear velocity, we are able to fractionate compounds within a given molecular weight range from any reaction mixture. For multiple fractionation 2 or more stripping columns can be operated in series using appropriate volumes of inert gas and linear velocities to achieve the desired overhead separation. If it is desired simply to remove the lower molecular weight components one stripping column will suffice and the finished ester product can be taken from the bottom of the stripper.

DRYING AND FILTRATION

Steam is the preferred carrier gas or stripping gas for our process. When it is used or when the neutralisation step follows the gas stripping step the product must be dried. The drying can be accomplished by subjecting the ester product to reduced pressure at a temperature above the boiling point of water or by sweeping the finished product with a dry inert gas. The product can then be filtered to obtain a high molecular weight ester product that is dry and free from any insoluble matter and haze.

By the procedure described it is possible to obtain purified products having very low colour, e.g. from 20 to 100 APHA and acid numbers less than 1. The initials APHA stand for American Public Health Association. The measurement of APHA colour on a Pt-Co scale is described on page 673 of "Technical Methods of Analysis" by R. C. Griffin (McGraw-Hill, 1927). The acid number is the number of milligrams of KOH required to neutralise the free acids in 1 gram of sample.

WHAT WE CLAIM IS:—

1. A method of purifying an ester, or linear polyester having a molecular weight of at least 400 and below 5000 which comprises passing a stream of the impure ester or polyester

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downwardly through at least one fractionating column having a gas-liquid contacting means and a stream of inert gas at a temperature of at least 100° C upwardly through the column at a linear velocity of from 3 to 100 feet per second, the purified ester or polyester being collected from the base of the column.

2. A method according to claim 1, said polyester having been produced by a process according to claim 4 or to claim 4 and any of claims 5 to 8 of the parent application 43340/62 1030213.

3. A method according to claim 1 or 2, the inert gas being superheated steam, nitrogen or methane.

4. A method according to any of claims 1 to 3, the temperature being at least 180° C.

5. A method according to any of claims 1 to 4, the velocity of the inert gas being from 3 to 6 feet per second or 0.9 metres per second.

6. A method according to any of the preceding claims in which the mixture is neutralised or washed substantially free of any acid and dried before or after said purifying.

7. A method of purifying an ester or polyester substantially as herein described.

8. A purified ester or polyester which has been produced by a method according to any of the preceding claims.

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